

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the hard court film which has the resin layer excellent in weatherability, transparency, solvent resistance, scratch-proof nature, and adhesion.

[0002]

[Description of the Prior Art]As a weatherproof film, plastic films, such as polyester film, are conventionally used as a substrate, and the thing which coated the coating material which uses as the main ingredients the polymer resin which added the ultraviolet ray absorbent on it, or the thing which scoured the ultraviolet ray absorbent to the high polymer film is known. . However, the weathering life of this kind of weatherproof film is short, and a white blush mark and a crack occur. The surface is soft, a crack is attached easily, a coat has a fault of a white blush mark and a crack occurring at the time of the insufficiency [flexibility] and post processing whose scratch-proof nature is not enough, and the actual condition cannot yet solve these problems by long-term weathering exposure.

[0003]

[Problem(s) to be Solved by the Invention]This invention uses as an offer plug the hard court film used suitably for outdoor ***** excellent in a weathering life, transparency, scratch-proof nature, flexibility, etc. in view of the actual condition of the above conventional technologies.

[0004]

[Means for Solving the Problem]The following means are used for this invention in order to solve this technical problem. Namely, a hard court film of this invention, An acrylic system monomer (meta) by which an ultraviolet absorption nature compound was added at least to at least one side of a polymeric film base, An acrylic system monomer (meta) to which a light stability compound was added, and three sorts of monomers with a polymerization nature

unsaturated compound which has a functional group have a resin layer which comes to carry out copolymerization, and in this resin layer, The bridge is constructed with a cross-linking compound reacted to this functional group, and it has a hard coat resin layer on this resin layer.

[0005]

[Embodiment of the Invention]. This invention was excellent in said technical problem, i.e., a weathering life, transparency, scratch-proof nature, flexibility, etc. About the hard coat film used suitably for outdoor *****. When inquire wholeheartedly, the copolymer-resin layer which consists of three sorts of specific monomers is made to construct a bridge further and a hard coat resin layer is made to laminate on it, it studies solving this technical problem at once also unexpectedly.

[0006]In this invention, with an acrylic (meta) copolymer. It is a copolymer of the acrylic system monomer (meta) which showed an acrylic acid series copolymer, a methacrylic acid system copolymer, etc., and added the ultraviolet absorption compound at least, the acrylic monomer (meta) which added the Sadamu Mitsuyasu compound, and the unsaturated compound which has a functional group, the ultraviolet absorption compound addition (meta-) acrylic system monomer used by this invention is excellent in copolymeric and ultraviolet absorption ability, and its heat resistance is good -- coloring -- it is few -- although -- selection -- it is desirable .

[0007]With an ultraviolet absorption nature compound, light energy with a wavelength of 400 nm or less is absorbed at least, With the compound which has the work which emits harmless thermal energy, phosphorescence, and fluorescence by very quick energy conversion, inhibits optical pumping of the impurity in polymer, and a photochemical reaction, and prevents degradation. Specifically, the ultraviolet absorption nature compound of organic systems, such as the thing of inorganic systems, such as a zinc oxide, titanium oxide, cerium oxide, and carbon black, a benzophenone series, a benzotriazol system, an oxalic anilide system, a cyanoacrylate system, a triazine series, and a benzoate system, can be used.

[0008]In this invention, as an acrylic system monomer (meta) which this ultraviolet absorption nature compound added, With the benzotriazol system compound which has in intramolecular an acrylic group in which copolymerization is possible (meta). 2-(2'-hydroxy-3'-tertiary butyl 5'-methylphenyl)-5-(2''-methacryloiloxy-ethyl) benzotriazol, 2 -(2'-hydroxy-5'-methylphenyl)-5-(2''-methacryloiloxy-ethyl) Benzotriazol, 2-(2'-hydroxy-5'-metacryloxy ethylphenyl)-2H-benzotriazol, 2-(2'-hydroxy-5'-metacryloxy ethylphenyl)-5-chloro-2H-benzotriazol, 2-(2'-hydroxy-5'-acryloyloxyethyl phenyl)-2H-benzotriazol, 2-(2'-hydroxy-3'-tertiary butyl 5'-acryloyloxyethyl phenyl)-5-chloro-2H-benzotriazol, etc. can be used.

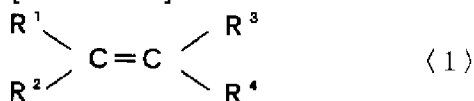
[0009]As acrylate (meta) which the light stability compound used in this invention added, By the reactant light stability compound addition (meta) acrylate of a hindered amine system with the piperidine ring by which steric exclusion was carried out. For example, 1,2,2,6,6-

pentamethyl 4-piperidyl methacrylate, 2, 2 and 6, and 6-tetramethyl 4-piperidyl methacrylate etc. can be used.

[0010]As a polymerization nature unsaturated compound which has a functional group, the compound expressed as follows, for example can be used.

[0011]

[Formula 1]



[0012]H, COOH, OH, and R² here R¹ H, CH₃, OH, COOH, and R³ H, COOR (R is an alkyl group of H or the carbon numbers 1-8), and R⁴, It is chosen out of either of the bases which make a main skeleton the hydrocarbon group of the straight chain shape which has COOR (R is an alkyl group of H or the carbon numbers 1-8) or a sulfonic group, an acid phosphate group, a halogen group, a hydroxyl group, a hydronaliumfurfuryl group, an amino group, and at least one or more kinds of bases chosen from an epoxy group.

[0013]As this compound, acrylic acid alkyl ester, such as alkyl acrylate and alkyl methacrylate, Acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, Carboxyl group content unsaturated compounds, such as crotonic acid, vinylsulfonic acid, Sulfonic group content unsaturated compounds, such as styrene sulfonic acid, diethylamino ethyl vinyl ether, 2-aminoethyl vinyl ether, 3-aminopropyl vinyl ether, An ether unsaturated compound containing amino groups, such as 2-aminobutylvinyl ether, beta-hydroxy acrylate, beta-hydroxy methacrylate, beta-hydroxypropyl acrylate, beta-hydroxypropyl methacrylate, polyoxy-ethylene-glycol mono- methacrylate, Hydroxyl group content unsaturated compounds, such as polyethylene polytetramethylene ether glycol mono- methacrylate, Amide bond content unsaturated compounds, such as acrylic ester which has amino groups, such as dimethylaminoethyl methacrylate and diethylamino ethyl methacrylate, acrylamide, methacrylamide, N-methylmethacrylamide, and N-n-butoxy methylacrylamide, Acid phosphate group content unsaturated compounds, such as acid phosphoxyethyl metacrylate and 3-chloro-2-acid phosphoxy propylmetacrylate, Halogen group content unsaturated compounds, such as 3-chloro-2-hydroxypropyl methacrylate, Epoxy group content unsaturated compounds, such as glycidyl acrylate and glycidyl methacrylate, An ether bond nature unsaturated compound which has hydroxyl groups, such as 5-hydroxypentylvinyl ether and 6-hydroxyhexylvinyl ether, An unsaturated compound which has hydronaliumfurfuryl groups, such as tetrahydrofurfuryl acrylate and tetrahydrofurfuryl methacrylate, Methylol group content acrylic acid amide compounds, such as N-methylolacrylamide and N-methylolmethacrylamide, Polyoxy-ethylene-glycol dimethacrylate, 1,3-butylene-glycol dimethacrylate, 1, 6-

hexanedioldimethacrylate, trimethylolpropane triacrylate, Although a compound chosen from a compound etc. which have two or more unsaturation groups in structures, such as trimethylolpropanetrimethacrylate and tetramethylolmethane triacrylate, one or more kinds can be used, It is not necessarily limited to these.

[0014]Furthermore, in addition to the above, the following monomers, for example, acrylonitrile, Mono- ***** of a methacrylonitrile, styrene, butylvinyl ether, maleic acid, and itaconic acid Dialkyl ester, A methyl vinyl ketone, VCM/PVC, a vinylidene chloride, vinyl acetate, vinylpyridine, vinyl pyrrolidone, alkoxysilane that has a vinyl group, polyester which has an unsaturated bond, etc. can also be used as a copolymerization ingredient.

[0015]Especially, in respect of the polymerization nature, paint film property, etc., alkyl methacrylate and alkyl acrylate are used preferably and, specifically, methyl methacrylate, ethyl acrylate, etc. can be used for a copolymer, for example. An acrylic monomer containing a carboxyl group, hydroxyl, a methylol group, an epoxy group, an alkoxy methyl group, an amino group, an amide group, etc. is also preferably used in respect of adhesion with a polymeric film base.

[0016]An acrylic copolymer in this invention (meta), An acrylic system monomer (meta) which added an ultraviolet absorption nature compound for an acrylic system monomer explained above to a main skeleton, It is characterized by being hybrid type acrylic polymer of a form which carried out copolymerization of the acrylic system monomer (meta) which added a light stability compound, namely, incorporated an ultraviolet ray absorbent and light stabilizer into acrylic polymer. A copolymerization ratio of an ultraviolet absorption nature compound addition (meta) acrylic system monomer occupied in this (meta) acrylic copolymer, Ten to 70% of the weight, it is 20 to 40 % of the weight more preferably, and a copolymerization ratio of a light stability compound addition (meta) acrylic system monomer is 1 to 30 % of the weight preferably, and its 5 to 20 % of the weight is still more preferred preferably from balance of weatherability, adhesion, endurance, coating nature, etc.

[0017]Although a number average molecular weight in particular of an acrylic copolymer in this invention (meta) is not limited, they are 0.4-40,000 preferably and 0.6-20,000 are more preferred from points, such as coating nature, the pliability of an enveloping layer, and endurance.

[0018]It is preferably preferred [glass transition temperature], although glass transition temperature in particular of an acrylic copolymer in this invention (meta) is not limited more preferably from points, such as the flexibility of a resin layer, and adhesion, to consider it as 30-60 ** preferably especially 20-70 ** 0-80 **.

[0019]furthermore -- as a reaction group of an acrylic copolymer in (meta-) this invention, a hydroxyl group is preferred and the hydroxyl value is a varnish base -- desirable -- 10-70 -- points, such as the solvent resistance of resin, adhesion, and processability, may be more

preferably sufficient as 20-50.

[0020]acid value -- a varnish base -- desirable -- 1-6 -- points, such as wettability with the upper coating material and adhesion, may be more preferably sufficient as 1-3.

[0021]A polymerization method of an acrylic copolymer used for this invention (meta) can be acquired, for example by methods, such as a radical polymerization, and is not limited in particular.

[0022]A functional group which exists in an acrylic (meta) copolymer with a cross-linking compound as used in the field of this invention, For example, it is a cross-linking compound for considering it as a resin layer which carries out heat crosslinking reaction to hydroxyl, a carboxyl group, a glycidyl group, an amino group, an amide group, a methylol group, etc., and has three-dimensional network structure eventually, It adds in order to raise adhesion with a high polymer film of a resin layer, tough nature, solvent resistance, a water resisting property, etc.

[0023]As this cross-linking compound, an isocyanate system compound, a melamine system compound, a urea system compound, epoxy compound, an amino compound, an amide system compound, an aziridine compound, an oxazoline compound, a silane coupling agent, etc. can be used, for example.

[0024]It is preferred to use an isocyanate system compound also in these in this invention from adhesion with a polymeric film base, the cross-linking of a resin layer, tough nature, etc. An isocyanate system compound has two or more isocyanate groups in one molecule, and is divided roughly into a compound of an aromatic system and an aliphatic series system. As a compound of an aromatic system, tolylene diisocyanate, diphenylmethane diisocyanate, Polymethylene polyphenyl polyisocyanate, naphthalene diisocyanate, Tolidine di-isocyanate, the Para Feni range isocyanate, etc. are used, and as a compound of an aliphatic series system, Hexamethylene di-isocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, hydrogenation xylylene diisocyanate, lysine diisocyanate, tetramethyl xylenediisocyanate, xylylene diisocyanate, etc. are used. In this invention, an aliphatic series system compound of non-yellow transformation is more preferably used from a weatherproof point.

[0025]To a methylol melamine derivative produced by condensing melamine and formaldehyde as a melamine system compound, as lower alcohol Methyl alcohol, Compounds which ethyl alcohol, isopropyl alcohol, etc. were made to react and were etherified, and those mixtures are used preferably. As a methylol melamine derivative, monomethylolmelamine, dimethylolmelamine, trimethylolmelamine, tetramethylolmelamine, pentamethylolmelamine, hexamethylolmelamine, etc. are used, for example.

[0026]As a urea system compound, a dimethylolurea, dimethylol ethylene urea, dimethylolpropylene urea, tetramethylolacetylene urea, 4-methoxy-5-dimethylpropylene urea

dimethylol, etc. are mentioned, for example.

[0027]As epoxy compound, they are specifically used by a poly epoxy compound, a diepoxy compound, and mono epoxy compound, and as a poly epoxy compound, For example, sorbitol, poly glycidyl ether, polyglycerol polyglycidyl ether, Pentaerythritol polyglycidyl ether, diglycerol polyglycidyl ether, As glycerol polyglycidyl ether, trimethylolpropane polyglycidyl ether, and a diepoxy compound, For example, neopentyl glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, Resorcinol diglycidyl ether, ethylene glycol diglycidyl ether, Polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, As polypropylene glycol diglycidyl ether, polytetramethylene glycol diglycidyl ether, and a mono epoxy compound, allyl glycidyl ether, 2-ethylhexyl glycidyl ether, phenyl glycidyl ether, etc. are used, for example.

[0028]As an amino compound, that etc. which formed diethylamino ethyl vinyl ether, 3-aminopropyl vinyl ether, 2-aminobutylvinyl ether, dimethylaminoethyl vinyl ether, and these amino groups into the ARUKI roll are used, for example.

[0029]As an amide compound, for example Acrylamide, methacrylamide, n-methylmethacrylamide, methylol-ized acrylamide, methylol-ized methacrylamide, ureido vinyl ether, beta-ureido isobutylvinyl ether, ureido ethyl acrylate, etc. are used.

[0030]Depending on independence and the case, two or more sorts of these cross-linking compounds may be used together. Although the kind uses quantity of a bridged compound to add, choosing it suitably, its 0.01 to 50 weight section is preferred to 100 copies of resin solid content, and its 0.2 to 30 weight section is more preferred.

[0031]since reaction velocity is promoted more for using a bridged compound and a catalyst together in this invention -- further -- good -- better -- it is adopted. For example, as a catalyst of an isocyanate system compound, an organic metal system and an amine system catalyst are preferred, dibutyltin dilaurate, stannous octoate, etc. are mentioned to the main things of an organic metal system catalyst, and a tertiary amine system, such as triethylenediamine, and amine salt are mentioned to an amine system catalyst. Although a bridge is constructed over an acrylic (meta) copolymer which added a bridged compound by heating, ultraviolet rays, an electron beam, etc. after applying to a film, a method by heating is usually adopted preferably.

[0032]In a resin layer of this invention, other various additive agents, for example, lubricant, a spray for preventing static electricity, a blocking-proof agent, a surface-active agent, a softening agent, a plasticizer, a color, paints, etc. may be added within limits which do not check an effect of this invention. When adding as lubricant bridge construction particles which especially consist of inorganic matter or an organic compound, since the slide nature of a polymeric film base improves and binding appearance and smoothness of a product at the time of processing become good, it is desirable.

[0033]Although a solvent in particular that furthermore uses an acrylic (meta) copolymer and a bridged compound of this invention for a coating material used as the main ingredients is not

limited, a solvent whose boiling point is 70-150 °C tends to be used for it from points, such as workability at the time of coating, and drying property before and behind hardening. As a concrete example, ester solvents, such as ketones, such as aromatic hydrocarbons solvents, such as toluene and xylene, methyl ethyl ketone, and methyl isobutyl ketone, ethyl acetate, and butyl acetate, can be used. Especially, ethyl acetate, methyl ethyl ketone, and toluene are good solvents, and are preferably used in respect of coating nature, the transparency of a coat, adhesion, etc. These solvents may be used together depending on independence and the case.

[0034]A polymeric film base in particular is not limited, but can use various plastic films, a plastic sheet, etc. For example, polyester film, a polycarbonate film, a polyvinylchloride film, a fluoro resin film, a polypropylene film, an acrylic film, etc. are used. Polyester film is especially preferred from optical and a viewpoint of intensity.

[0035]With polyester of polyester film of this invention. Are an ester bond a general term of polymers made into main joining chains of a main chain, and as desirable polyester, What uses as a major constituent at least one sort of constituents chosen from ethylene terephthalate, ethylene-2,6-naphthalate, butylene terephthalate, the ethylene- alpha, the beta-bis(2-chlorophenoxy)ethane- 4, 4'-dicarboxylate, etc. is used. Although one sort of these constituents may be used, two or more sorts may be used together or any may be sufficient, when quality, economical efficiency, etc. are judged synthetically especially, polyester which uses ethylene terephthalate as a major constituent is preferred. a dicarboxylic acid component and a diol component of further others [polyester / these] -- less than 20 mol % -- copolymerization may be carried out.

[0036]As for polyester film which uses the above-mentioned polyester, it is preferred that biaxial orientation is carried out in the state where a quick adhesive agent was applied. A biaxial orientation polyester film is respectively extended about 2.5 to 5 times a longitudinal direction and crosswise in a polyester sheet or a film in a state where it does not extend, performs the stress relief heat treatment, makes crystal orientation complete, and refers to what shows a pattern of biaxial orientation according to a wide angle X diffraction.

[0037]When forming a resin layer on the surface of a polymeric film base, since adhesion with a polymers film surface is improved, spreading nature not only improves by performing a surface treatment and under coat processing, but it can use more preferably. A method (inside of air, nitrogen, and carbon dioxide, rare gas middle class) publicly known as a surface treatment, for example, corona discharge treatment, plasma (glow discharge) processing (high voltage, low pressure), high frequency sputter etching processing, etc. are performed, and a disposal method which makes a high energy particle collide with a polymers film surface is adopted. On the other hand, alkali solution processing of carrying out the dipping of the plastic film to ammonia liquor of metallic sodium or a tetrahydrofuran solution of a sodium

naphthalene complex is used for a chemical treatment.

[0038]A quick adhesive agent which consists of an organic compound which has an atom group containing oxygen and/or nitrogen as under coat processing may be applied. As an atom group containing oxygen and/or nitrogen, an amino group, an imino group, a carboxyl group, hydroxyl, a carbonyl group, an ether group, an epoxy group, an isocyanate group, an amide group, a urethane group, an ester group, a urea group, a cyano group, etc. can be illustrated. As an organic compound which has such an atom group, Polyester, polyamide, a polyvinyl acetal, polyvinyl chloride, Polyester acrylates, polyimide, polyurethane, polyurethane acrylate, Although polycarbonate, polystyrene, a polymethylpentene, polyolefine, halogenation polyolefine, alkyd resin, polyamidoimide, polyvinyl alcohol, silicic acid resin, etc. are used, It is desirable as a film which adhesion of what carried out the under coat of the constituent which consists of a copolymer which made hydrophilic group content polyester resin graft-ize an acrylic compound, and a bridged compound improved, and was especially excellent in endurance, such as resistance to moist heat and boiling water resistance.

[0039]As for thickness of these under coats, it is preferably good $0.01 - 2 \text{ g/m}^2$ and that it is $0.1 - 1 \text{ g/m}^2$ still more preferably. That is, it is difficult to apply uniformly, if this thickness is thinner than 0.01 g/m^2 , and if 2 g/m^2 is exceeded, it becomes difficult to acquire the transparency of an enveloping layer which carries out coating on this, flexibility, etc., and it is not preferred.

[0040]In the case of a surface treatment, processing strength in particular is not limited but can consider it as a desired value according to a use, but. It is good for a film measured based on JIS-K6768 as a rule of thumb of processing strength to get wet, and to set preferably 40 dynes/cm or more of indices to cm in 45 dynes /or more still more preferably.

[0041]Although thickness in particular of a polymeric film base is not limited, it is 20-300 micrometers still more preferably 10-500 micrometers preferably from points, such as a mechanical strength, thermal conductivity, and workability. An obtained film can be pasted together by a publicly known method, and it can also be considered as a still thicker film.

[0042]Although thickness in particular of a resin layer in this invention is not limited, they are 0.5 micrometer - 15 micrometers preferably. When using polyester film as a polymeric film base and about five or less years of weathering life is generally required, Being referred to as 2-4 micrometers still more preferably 1-8 micrometers preferably when a weathering life for five years or more and about ten years or less is required, It is preferably more preferred from fields, such as flexibility as a weatherproof film, curl-proof and crack-proof nature, transparency, a mechanical strength, and processability, to be referred to as 4-6 micrometers still more preferably 3-15 micrometers.

[0043]The surface of a resin layer gets wet, and when an index prevents a crack white blush mark under influence of moisture at the time of an outdoor exposure, it is preferably good that

42 dynes/cm or less are 38 dynes/cm or less still more preferably.

[0044]the uses with main total light transmittance -- high -- it is preferably good from being objects for protective films, such as transparent glass and a methacrylic resin board, that it is not less than 85% still more preferably not less than 80%.

[0045]As for a bridge construction index of a resin layer, it is preferred that it is 0.15 or less from solvent resistance, chip box-proof milkiness, a weathering white blush mark, processability, etc.

[0046]Next, a case where polyester film is used as a substrate about a painting method of a resin layer of this invention is explained. Although not limited in particular for a coating method, a coating material which uses as the main ingredients the above-mentioned (meta) acrylic copolymer which carried out concentration adjustment, and a bridged compound to 10 to 40% Gravure coating, After coating using various kinds of publicly known coat methods, such as a reverse coat, a kis coat, a die coat, and a metering bar coat, it is made to dry several seconds - several minutes under 50-180 °C heating conditions.

[0047]The same desirable thing as a use solvent in an acrylic (meta) copolymer is at best still more preferred, and a solvent used for concentration adjustment has preferred ethyl acetate in respect of coating nature.

[0048]It is more preferred after the above-mentioned end of a painting process to heat-treat for more than four days at 35-60 °C more preferably for more than two days at 30-80 °C in respect of bridge construction of a resin layer, adhesion, a weathering white blush mark, etc.

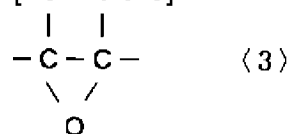
[0049]As a compound which contains an epoxy group and a silanol group in intramolecular among silicon compounds of a hard court resin layer on a resin layer used by this invention, it is the chemical formula 2. [0050]

[Formula 2]



[0051](However, X¹, the following chemical formula 3) [0052]

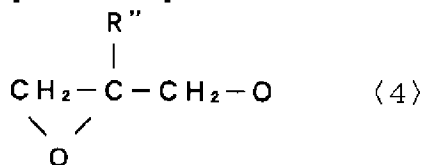
[Formula 3]



[0053]As for the alkyl group of C₁ - C₆, an alkoxy group or an aryl group, and n, the integer of 0-2 and b of a ***** group and R¹ are [2 or 3a] compounds expressed with the integer of 1-6.

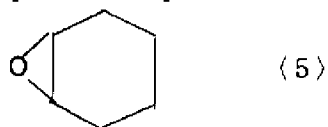
[0054]Here, as a basis containing the chemical formula 3, it is the following chemical formula 4, for example. [0055]

[Formula 4]



[0056](-- the compound by which R² is expressed with hydrogen or methyl group) among a formula, and the chemical formula 5 [0057]

[Formula 5]



[0058]It can come out and the compound etc. which are shown can be adopted.

[0059]As a silicon compound, the compound which contains a glycidyl ether group and a silanol group in intramolecular is used preferably.

[0060]As a concrete example of a silicon compound, although the hydrolyzate of gamma-glycidoxy propyl trialkoxysilane, gamma-glycidoxy propylmethyl dialkoxy silane, and beta-(3,4-epoxycyclohexyl) ethyl trialkoxysilane can be mentioned, In this invention, it is not limited to these.

[0061]Hydrolysis of these silicon compounds can be easily performed by carrying out addition stirring of the aqueous acids, such as water, chloride, or sulfuric acid. Usually, hydrolysis of a silicon compound is performed by adding acid water at once or gradually in the above-mentioned silicon compound. Since organic carboxylic acid, such as alcohol, alkoxy alcohol, and acetic acid, etc. generate when hydrolyzing, hydrolyzing with a non-solvent is possible. It may hydrolyze, after hydrolyzing, respectively, mixing and mixing two or more sorts, when a silicon compound is two or more sorts.

[0062]An epoxy compound used in a hard court resin layer of this invention is used in order to mainly give flexibility. A polyolefin system epoxy resin compounded by a hyperoxidation method as an epoxy compound, for example, Poly glycidyl ester obtained from cyclopentadieneoxide or hexahydrophthalic acid, and epichlorohydrin, Polyhydric phenol or (poly) ethylene glycol, such as bisphenol A, catechol, resorcinol, (Poly) Propylene glycol, neopentyl glycol, glycerin, trimethylolpropane and pentaerythritol -- it and, [jig-lycee-] Poly glycidyl ether obtained from polyhydric alcohol and epichlorohydrin, such as sorbitol, A cyclic epoxy resin, epoxidized vegetable oil, novolac type phenol resin and epoxy novolak resin obtained from epichlorohydrin, Although a copolymer with acrylate system monomers, such as an epoxy resin obtained from phenolphthalein and epichlorohydrin and also glycidyl methacrylate, and methyl methacrylate, or styrene, etc. are used, in this invention, it is not

necessarily limited to these.

[0063]As for content of a silicon compound in this resin layer, and an epoxy compound, it is desirable for per resin-solid-content 1 weight section and a silicon compound to be 0.20 to 0.80 weight sections, and its 0.40 to 0.60 weight section is especially preferably good 0.30 to 0.70 weight section more preferably. As for an epoxy compound, it is desirable that it is 0.20 to 0.80 weight section, and its 0.40 to 0.60 weight section is especially preferably good 0.30 to 0.70 weight section more preferably. If there are few silicon compounds than a mentioned range, scratch-proof nature runs short, and when large, a tendency inferior to flexibility nature is shown. When there is less content of an epoxy compound than a mentioned range, it is inferior to flexibility, and when large, a tendency for scratch-proof nature and transparency to fall is shown.

[0064]In this invention, a metal complex is especially used preferably from an ease of handling, and a point of a cure rate as a catalyst which promotes reactions, such as an epoxy compound in this resin. It is also in various metal complexes and an aluminium compound expressed with the following general formula is used especially preferably.

[0065]aluminum- Y_m and $Z_{(3-m)}$ (however, Y -- OL (L is an alkyl group of $C_1 - 6$.) Z is general formula $M^1COCH_2COM^2$ or $M^3COCH_2COOM^4$ (M^1). each of M^2 , M^3 , and M^4 is at least one chosen from a combination child originating in a compound shown by an alkyl group of $C_1 - 6$, and m is an integer of 0-3.

As an example of this compound, aluminum iso-propoxide, Aluminum ethoxide, aluminum tert-butoxide, aluminum acetylacetonate, *****-***** acetoacetate ****-*****
Aluminum di-n-butoxide-mono-ethylacetoacetate, Aluminum di-iso-propoxide-mono-methylacetoacetate, Aluminum di-sec-butoxide-mono-ethylacetoacetate, aluminum *-
*****-****- methylacetoacetate, etc. are preferably used from viewpoints of an effect as solubility, stability, and a curing catalyst to a constituent, etc. The number of these compounds may be one, and two or more sorts may use them, mixing.

[0066]An addition of this metal complex has 0.0001 to 0.5 preferred weight section per epoxy compound 1 weight section, especially, if 0.0005 to 0.2 weight section is suitable and there are preferably than this, it becomes insufficient in an effect, and on the other hand, an addition of this metal complex shows a tendency which produces defects, such as a fall of the transparency of a coat or resin, and a waterproof fall, by more than this. [few]

[0067]Silicon compound (I) which contains an epoxy group and a silanol group in such intramoleculars in this invention, A coating composition which contains at least a compound which consists of epoxy compound (II) and metal complex (III) is melted in a solvent, After coating a resin layer with the usual coating method on a film base which carried out coating, a weatherproof film which has a hard court function can be manufactured by heating, drying and

making a coating composition react. Radiation etc. can be used and a compound in a resin layer can also be made to react if needed.

[0068]A resin layer containing a silicon compound is not what is limited only to a reactant which consists of a silicon compound, a (II) epoxy compound, and a (III) metal complex which contain an epoxy group and a silanol group in (I) intramolecular, Besides a compound which consists of these (I)s, (II), and (III). for example, tetra alkoxy silane and doria -- organic silane compounds, such as a RUKOKISHI alkyl silane, and hydrolyzate of those, and silica -- resin, such as inorganic compounds, such as sol, or polyvinyl alcohol, and polyacrylamide, may be added. Various additive agents, such as lubricant, a spray for preventing static electricity, a blocking-proof agent, a color, paints, a photosensitizer, and a surface-active agent, can be added if needed. By adding lubricant, such as silica or bridge construction polystyrene, especially, a slide of a film surface can improve and binding appearance and smoothness of a product at the time of manufacture can be improved.

[0069]In order to raise productivity and processability of a hard court resin layer, a cationic initiator may be suitably added to a resin layer. This cationic initiator has played a role which promotes an epoxy group of a silicon compound, and a reaction of an epoxy compound.

[0070]As this cationic initiator, what starts a reaction with heat and/or radiation can be used, For example, aromatic onium salt, such as sulfonium salt, such as a cinnamyl type, a naphthyl type, and a benzyl type, ammonium salt, phosphonium salt, and iodonium salt, etc. are used preferably. What mixed two or more kinds or mixed an auxiliary agent may be used if needed. It may be used after making it dissolve in a solvent.

[0071]Preferably an addition of this cationic initiator per epoxy compound 1 weight section to intramolecular 0.0001 to 0.5 weight section, Especially, when 0.0005 to 0.2 weight section is preferably suitable and there are too many additions of a cationic initiator, a tendency which produces defects, such as a fall of the transparency of a coat or resin and a waterproof fall, is shown.

[0072]If 0.1-10 micrometers is suitable for coat thickness of a hard court resin layer and are preferably thinner than this especially preferably 0.05-30 micrometers, it runs short of the scratch-proof nature of a layered product, and a tendency for workability to worsen if thicker than this, or to become easy to cause blocking is shown.

[0073]When using heat as means forming of a resin layer by this invention, heating conditions are 100-200 ** preferably, but 50-170 ** is more preferably suitable. From this, at low temperature, since reaction velocity of a silicon compound is slow, productivity worsens, and fault that appearance of a film worsens with degradation of a substrate, or on the other hand a cationic initiator decomposes at an elevated temperature from this arises.

[0074]Although electromagnetic waves, such as alpha rays, a beta ray, a gamma ray and ultraviolet rays, and X-rays, and an electron beam are mentioned as radiation used by this

invention, a field of efficiency to simplicity and UV irradiation are desirable.

[0075]UV irradiation is preferably performed on wavelength of 250-400 nm, and a low pressure mercury lamp, a medium-voltage mercury-vapor lamp, a high-pressure mercury-vapor lamp, a metal halide lamp, a xenon lamp, a carbon arc lamp, an electron beam, etc. are used as a light source.

[0076]A hard court film of this invention is used suitably for uses as which weatherability, transparency, scratch-proof nature, etc. are required over a long period of time, such as an automotive application and a film for outdoor ***** construction-related [various].

[0077]

[Example]Although an example and a comparative example are used for below and this invention is explained to it, this invention is not limited to these.

[0078]The weighted solidity of this invention in an example and a comparative example is based on the measuring method and valuation basis which are shown below.

[0079](1) Using the weatherproof accelerated test ultraviolet-ray-degradation accelerated test machine (eye super UV tester SUV-W131: made by the Iwasaki Electric Co., Ltd.), the exposure cycle test was done on condition of the following, and the generation state of the adhesion of a film, b value, a crack, and bubble was evaluated.

[0080]It was considered as the 1 cycle exposure cycle in 12 light 8-hour (UV illumination: 100 mW/cm² temperature and humidity : 60 ** x 50%RH) => DEYU [4 hours] (temperature and humidity: 35 ** x 100%RH dew condensation) hours, and the characteristic before and behind 12 cycle exposure was evaluated.

[0081](b) Adhesion cellophane tape exfoliation estimated. The cellophane tape by Nichiban Co., Ltd. of 10-mm width was stuck on the enveloping layer, and the survival rate of the enveloping layer after exfoliating in the direction of 45 degree was judged visually.

[0082]

O :survival-rate 100%** : ** more than 50% x : yellowing of a ** less than 50% (**) film -- according to JIS K-7105, it asked for the degree of yellowing of a film with b value using SM color computer by Suga Test Instruments Co., Ltd. The degree of yellowing is small preferred so that b value is low.

[0083](**) The optical microscope made from Crack Japan Optics was used, and the surface state of the irradiation surface (enveloping layer side) was observed and judged by one 200 times the magnification of this.

[0084]O : with no crack.

[0085]** : The crack has occurred slightly.

[0086]x : The crack has occurred on the whole surface.

[0087](**) Based on JISK-7105, it measured using the direct reading Hayes computer by Hayes Suga Test Instruments Co., Ltd. Transparency is well preferred so that Hayes is low.

[0088](2) Based on JIS K-7105, it measured using the direct reading Hayes computer by total-light-transmittance Suga Test Instruments Co., Ltd. Transparency is well preferred so that light transmission is high.

[0089](3) The film surface was rubbed by wear-resistant steel wool #0000, the crack stuck, and the following standard estimated condition.

[0090]: Even if it rubs strongly, a crack hardly sticks.

[0091]**: If it rubs strongly, a crack will stick.

[0092]x: A crack also attaches weak friction.

[0093](4) According to JIS K-5400, it measured using the pencil hardness HEIDON (product made from New East Science).

[0094](5) The film cut in the size of 10x10 cm of curl was placed on the glass plate, the relief state of both ends was observed, and the height from a flat surface was measured.

[0095](6) 160-180 degrees of hard court films were bent to the opposite hand of the refraction crack examination resin layer, and the entering state of the crack of the refraction portion after 1 stroke ** makes a bend portion a rubber coated roller with a weight of 1 kg was observed with the magnifying glass 25 times the magnification of this, and was judged.

[0096]The judgment was performed on the following standard.

[0097]O : with no crack.

[0098]**: The crack generation is carried out slightly.

[0099]x: The crack generation is carried out to the whole surface.

[0100](7) The solvent resistance cotton swab was impregnated in the solvent, and the rubbing test was done.

[0101]What O and change are regarded as in what change is not regarded as by the enveloping layer by ten strokes was made into x.

[0102](Example 1) 2-(2'-hydroxy-3'-tertiary butyl 5'-methylphenyl)-5-(2"-methacryloiloxy-ethyl) benzotriazol, 1,2,2,6,6-pentamethyl 4-piperidyl methacrylate, To the solvent solution of 90 % of the weight of solid content diluted with ethyl acetate, the acrylic copolymer (glass transition temperature of 30 **; "you double" TP-10TR) which consists of a three-sort monomer of beta-hydroxymethyl methacrylate. [by NIPPON SHOKUBAI Co., Ltd.] The uniform coating liquid of 20 % of the weight of solids concentration which mixed the cross-linking compound (the product made from Japanese Chemically-modified Paint; isocyanate system XDI adduct type) 10%, After applying to 50-micrometer-thick biaxial extension polyester film ("lumiler by Toray Industries, Inc. "T60) with a metering bar, it was made to dry for 2 minutes at 140 ** in hot wind circle method oven, and the 5-micrometer-thick resin layer was provided.

[0103]50 copies of hydrolyzates (58% of solid content) produced by 0.01N hydrochloric acid aqueous solution hydrolyzing gamma-glycidoxypopyltrimetoxysilane on it are dissolved in 253 copies of mixed liquor of isopropyl alcohol / n-butyl alcohol / toluene, Applied to this the

uniform coating liquid which added 50 copies of epoxy compounds ("DINA call" EX-314 by Nagase& Co., Ltd.), and ten copies of aluminum acetylacetonate using the metering bar, and dry for 2 minutes, it was made to harden at 130 **, and the 3-micrometer-thick hard court was formed.

[0104]The obtained evaluation test result is shown in Table 1.

[0105](Example 2) On the same resin layer as Example 1, gamma-glycidoxypyrroltrimetoxysilane, 50 copies of hydrolyzates (58% of solid content) produced by 0.01N hydrochloric acid aqueous solution hydrolyzing are dissolved in 253 copies of mixed liquor of isopropyl alcohol / n-butyl alcohol / toluene, To this, 50 copies of epoxy compounds ("DINA call" EX-314 by Nagase& Co., Ltd.), the thermosetting cationic initiator (3 Japanese Federation of Chemical Industry Workers' Unions make "SI-60L" (33% of solid content).) after adding ten copies of aluminum acetylacetonate It applied using the metering bar, and at 130 **, it dries for 2 minutes, the uniform ointment which added five copies of sulfonium salt system compounds was stiffened, and the 3-micrometer-thick hard court was formed. The obtained evaluation test result is shown in Table 1.

[0106](Example 3) On the same resin layer as Example 1, gamma-glycidoxypyrroltrimetoxysilane, 50 copies of hydrolyzates (58% of solid content) produced by 0.01N hydrochloric acid aqueous solution hydrolyzing are dissolved in 253 copies of mixed liquor of isopropyl alcohol / n-butyl alcohol / toluene, To this, 50 copies of epoxy compounds ("DINA call" EX-314 by Nagase& Co., Ltd.), After adding ten copies of aluminum acetylacetonate, the uniform coating liquid which added 1.0 copy of photoresist cationic initiator (Asahi Denka Kogyo [K.K.] make "ADEKAOPUTOMA SP-170": 50% of solid content; sulfonium salt system compound), After applying using the metering bar and drying for 2 minutes at 130 **, ultraviolet rays were irradiated with and stiffened and the 3-micrometer-thick hard court was formed. The obtained evaluation test result is shown in Table 1.

[0107](Comparative example 1) To 50-micrometer-thick biaxial extension polyester film ("lumiler by Toray Industries, Inc. "T60). Use ethyl acetate as a diluent solvent and an acrylic (meta) copolymer ("you double" TP-10TR; glass transition temperature of 30 **) by a solid content weight ratio 90%, [by NIPPON SHOKUBAI Co., Ltd.] The uniform coating liquid of 20% of the concentration for which the cross-linking compound (product isocyanate system XDI adduct type made from Japanese Chemically-modified Paint) was mixed 10% was dried for 2 minutes at 140 ** in hot wind circle method oven after spreading the metering bar, and the 5-micrometer-thick resin layer was provided. The obtained evaluation test result is shown in Table 1.

[0108](Comparative example 2) On the same resin layer as Example 1, applied the inorganic hard court agent of a siloxane system, and dry for 2 minutes, it was made to harden at 130 **, and the hard court was laminated. The obtained evaluation test result is shown in Table 1.

[0109]

[Table 1]

表 1

		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
耐 候 性	密着性	○	○	○	○	△
	黄変 (b 値)	1.2	1.2	1.1	1.1	1.1
	亀裂	○	○	○	○	△
	ヘイズ (%)	1.5	1.5	1.5	1.4	1.3
全光線透過率 (%)		91.2	91.1	91.0	91.0	91.2
耐摩耗性		○	○	○	△	○
鉛筆硬度		2 H	2 H	2 H	B	2 H
カール (mm)		0	0	0	0	2

[0110]In respect of weatherability, abrasion resistance, hardness, or curl, as compared with the thing of Examples 1-3, the thing of the comparative examples 1 and 2 is inferior so that clearly from Table 1.

[0111]

[Effect of the Invention]According to this invention, in weatherability, transparency, scratch-proof nature, adhesion, and all the curl-proof, it can be satisfied, and the car and the film for outdoor ***** construction-related [various] as which five years or more of weathering life is required especially can be provided.

[Translation done.]